TECHNICAL REPORT 23

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INTERPRETATION OF EXPERIMENTS ON DISSOCIATIVE ATTACHMENT OR IONIZATION OF MOLECULES*

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The purpose of this letter is to point out an error in the method normally used to relate the measured kinetic energy of fragment ions to the total energy released in dissociative reactions. In particular, an appreciation of this error leads to an understanding of the discrepancy existing in the literature between the photodetachment measurement[1] of the electron affinity of atomic oxygen, and the value obtained from electron beam experiments in O_2[2].

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*This work has been supported in part by the Advanced Research Projects Agency through the Office of Naval Research.

(1) L. M. Branscomb, D. S. Burch, S. J. Smith, S. Geltman, Phys. Rev. 111, 504, (1958), and for a review, see L. M. Branscomb, Atomic and Molecular Processes, Chapter 4, edited by D. R. Bates, Academic Press, 1962.

(2) G. J. Schulz, Phys. Rev. 128, 178 (1962), finds that an application of eqn. (1) to electron beam experiments leads to a value for the electron affinity of atomic oxygen of 2.0 eV, whereas the value determined from photodetachment experiments is 1.46 eV.

In the past, the effect of the thermal motion of the target molecule in a reaction of the type $e + XY \longrightarrow X^- + Y$ has been assumed to be negligible. With this assumption, conservation of energy requires that the kinetic energy given to the fragments be $E_R = V_e - (D-A)$. The additional requirement that momentum be conserved leads to the relation[3]

$$E_o = (1 - \beta) \left[V_e - (D - A) \right] \qquad (1)$$

In the above V_e is the electron energy, D is the dissociation energy of XY, A is the electron affinity of the fragment X, E_o is the kinetic energy of the ion X^-, and $\beta = \frac{m}{M}$ where m is the mass of X^- and M that of the target molecule XY.

The experimental arrangements employed in the study of dissociative processes by electron beams are varied but all methods attempt to determine the ion energy produced by electrons of known energy, by measuring the maximum retarding potential $E_{r\ max}$ which the ions are able to penetrate. Any apparent

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(3) The reasoning outlined above was first applied by W. W. Lozier, Phys. Rev. 36, 1285 (1930) to the interpretation of measurements of H^+ produced from H_2. Since that time it has been applied by many workers, especially to dissociative attachment studies, where, given the value of D the data provides a determination of A, the electron affinity. See also J. T. Tate and W. W. Lozier, Phys. Rev. 39, 254 (1932), and for a review, see H. D. Hagstrum, Rev. Mod. Phys. 23, 185 (1951).

spread in ion energies above that expected from the spread in electron energy is ascribed to the ions having entered the retarding field at various angles, it being assumed that the maximum ion energy measured $E_{r\ max}$ corresponds to the true ion energy, E_o, given by equation (1). A linear extrapolation of a plot of $E_{r\ max}$ vs. V_e to zero $E_{r\ max}$ with a slope determined by eqn. (1) has been interpreted in the past as leading to the proper value of (D-A). It will be shown that this procedure is erroneous, due to the neglect of the thermal motion of the target molecule, leading to a value of A which is likely to be too large.

Theory

The energy of thermal motion is generally very much smaller than the other terms in the energy equation, and its neglect may be justified on this basis. It may be shown, however, that the random direction of the momentum of thermal motion causes a significant spread in ion energies.

This effect may be understood in terms of the following simple argument. In the absence of thermal motion of the target XY the ion X^- will have a velocity $v_o = \left(\frac{2E_o}{m}\right)^{1/2}$ where E_o is given by equation (1). If we now assume that all the gas molecules have the same thermal velocity v_T, random in direction, we may calculate the total spread in ion energies by considering the two extreme cases where v_T is in the same direction as v_o, and opposite to it. In order to conserve the extra momentum the ion velocity becomes $(v_o + v_T)$ and $(v_o - v_T)$ in the two cases. The total spread in ion energies is therefore $\frac{1}{2} m (4 v_o v_T)$. The temperature of our uni-speed gas may

be defined by $\frac{1}{2} M v_T^2 = \frac{3}{2} kT$ in which case the total ion energy spread may be written as $(24\ \beta kTE_o)^{1/2}$.

A rigorous treatment of the problem involving suitable integration over the Maxwellian Distribution of thermal velocities of XY leads, with the assumption that $E_o \gtrsim 3kT$, to the ion energy distribution.

$$\frac{dN}{N} = \left(\frac{1}{4\pi\beta kTE_o} \right)^{1/2} e^{-\frac{1}{\beta kT}\left(E^{1/2}-E_o^{1/2}\right)^2} dE \quad . \tag{2}$$

The width at half maximum of this distribution is given by[4]

$$W_{1/2} = (11.0\ \beta kTE_o)^{1/2} \tag{3}$$

For O^- from O_2 at 350°K and E_o = 2 eV, $W_{1/2}$ is 0.56 eV, and we conclude that ions are produced with energies significantly greater than E_o. Therefore the assumption normally made that the maximum ion kinetic energy measured corresponds to E_o is erroneous.

Comparison with Experiment

Attempts to re-interpret existing experimental data in the light of equation (2) are rendered difficult by the following considerations.

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(4) An experiment designed to measure the dependence of $W_{1/2}$ on E_o and on T is in progress and preliminary results show that the measured half width, $W_{1/2}$, of O^- from O_2 decreases with a decrease in gas temperature. Details of the experiment will be published in due time.

i. The concept of a "maximum ion kinetic energy" becomes meaningless due to the high energy tail of expression (2). In practice, of course, this tail will at some point disappear into the noise associated with the particular detector system employed.

ii. The actual shape of the tail in the retarding curve observed in a given experiment will depend on the angular distribution of the dissociation products[5], and on the collection system geometry.

iii. The gas temperature in the collision chamber has not usually been measured.

It is nevertheless instructive to compare the shape of the retarding curve expected on the basis of the present theory, and some assumptions regarding (ii) and (iii) above, with experimental data. For this purpose we take two sample retarding curves for O^- produced from O_2 by electron impact, measured by Schulz[6] in a tube of cylindrical geometry having a large collection angle, assumed for the purpose of this comparison to be 180^o. We assume also that the ions have an isotropic distribution and that $T = 350^oK$. The ratio of the current collected with a retarding voltage E_r present, to that collected without retardation is then given by

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(5) G. H. Dunn, Phys. Rev. Letters 8, 62 (1962).

(6) G. J. Schulz, Phys. Rev. 128, 178 (1962). The retarding curves used here are not explicitly shown in the above reference; from such a curve the "maximum kinetic energy" was determined, providing one point of Fig. 10 of the reference.

$$\frac{I_r}{I_o} = \left(\frac{1}{4\pi\beta kTE_o} \right)^{1/2} \int_{E_r}^{\infty} \left(1 - \frac{E_r}{E}\right)^{1/2} e^{-\frac{1}{\beta kT}(E^{1/2} - E_o^{1/2})^2} dE. \qquad (4)$$

Performing the integration numerically for suitably spaced values of E_r allows us to plot the retarding curve $\frac{I_r}{I_o} = f(E_r)$. The result is shown as the full curve in Figure 1. The points are experimental, taken under different circumstances but for the same electron energy, $V_e = 6.8$ eV. The value of E_o used in calculating the full curve is obtained from equation (1) using this value of V_e, D = 5.11 eV and A = 1.5 eV.

The agreement is probably to some extent fortuitous, but serves to show that experimental data which, using previously accepted methods of interpretation led to an electron affinity of 2.0 eV, are in fact consistent with a value of 1.5 eV.

The above method of comparison of experiment and theory is tedious to perform due to the numerical integration involved. A more direct method of comparison is to calculate the retarding voltage $E_{r\ max}$ corresponding to the published values of "maximum measured ion kinetic energy", for various values of V_e. To do this we need to know also the procedure adopted by the experimenter in determining the maximum measured ion energy from the retardation curve. We therefore proceed in the following way.

It is reasonable to assume that the difference between $E_{r\ max}$ and E_o is proportional to the half-width of the ion energy distribution, given by equation (3). Let us therefore write

$$E_{r\ max} = E_o + \alpha\ (\beta kT\ E_o)^{1/2} \qquad (5)$$

where α is a parameter depending on the procedure adopted in picking off $E_{r\ max}$ from the retarding curve, and on the angular distribution of the ions. These latter quantities are constant for a given reaction studied in a given apparatus, and with these restrictions we shall assume that α is a constant.

One of the methods used by Schulz[6] in determining the maximum measured ion energy was to linearly extrapolate the retarding curve to the axis. Applying the same treatment to the theoretically calculated retarding curve of Fig. 1 gives $\frac{E_{r\ max}}{E_o} \simeq 1.20$, for this particular case. Solving (5) for α we obtain $\alpha = 2.0$. It can be shown that this value of α corresponds to taking $E_{r\ max}$ to be such that 10% of the ions have $E > E_{r\ max}$.

Combination of equations (1) and (5) using $\alpha = 2.0$ gives

$$\frac{E_{r\ max}}{1 - \beta} = E_R + \left(\frac{4\beta kT}{1-\beta}\right)^{1/2} E_R^{1/2} \qquad (6)$$

Three plots of this equation are shown in Fig. 2. The dashed straight line of unit slope passing through the origin, obtained from the present theory by setting $T = 0$, corresponds to the theory used in all previous work. The two full curves employ $T = 350^{\circ}K$ and $\beta = 0.5$, corresponding to a homonuclear diatomic molecule, in one case, and $\beta = 0.055$ corresponding to production of H^- from H_2O in the other.

The open circles are experimental points for O^- produced from O_2, being the same data as plotted in Fig. 10 of reference 6. The experimental E_R scale is determined from the measured V_e scale, assuming D = 5.11 eV and A = 1.5 eV. The agreement of experiment with the theoretical curve over the whole range of the points is seen to be, if anything, better than that obtained by fitting to the points a straight line of unit slope. Such a line is shown in the figure, and has been interpreted in the past as leading to a value of A which is too large by 0.5 eV.

The closed circles are experimental measurements on H^- from H_2O, being the same data as Fig. 11 of reference 6, and are plotted on the E_R scale by taking D = 5.11 eV and A = 0.74 eV. This reaction is of interest since it shows clearly the dependence of the energy correction arising from the present theory on β, the ratio of the ion mass to the target molecule mass. The correction is seen to be very small in this case.

Conclusions

1) The method of analysis normally applied in deducing electron affinities from measured ion energies resulting from dissociative attachment is, in general, only approximate. The error involved increases with the temperature of the target gas[7], with the ion energy, and with β, the ratio of the ion mass to the target molecule mass, leading to values of the electron affinity which

(7) In an experiment on H^- formation from H_2, (G. J. Schulz, Phys. Rev. 113, 816 (1959)), the gas was cooled to liquid nitrogen temperature in order to eliminate the H_2O impurity. This fortuitous experimental procedure reduced the error resulting from the thermal spread.

are likely to be too high. In particular, one is able to understand the discrepancy existing between the values of $A(O^-)$ determined by electron impact methods, and that determined by photo-detachment studies[1]. We may note, however, that the present arguments do not affect the interpretation of the appearance potential of truly zero energy ions[8].

2) In dissociative reactions involving production of positive ions, the ion energy distribution is expected to be broader than that predicted simply on the basis of the Franck-Condon principle, the broadening being greatest on the high energy side of the distribution.

The authors are indebted to the members of the Atomic Physics Group of the Westinghouse Research Laboratories for stimulating discussions in connection with this work.

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(8) Application of the present theory leads to an understanding of many of the anomalies in the literature on electron affinity determinations by electron impact studies. A notable exception is that of O^- from CO_2[6]; in this case the onset of zero kinetic energy ions has been found to be consistent with an electron affinity of 2.0 eV.

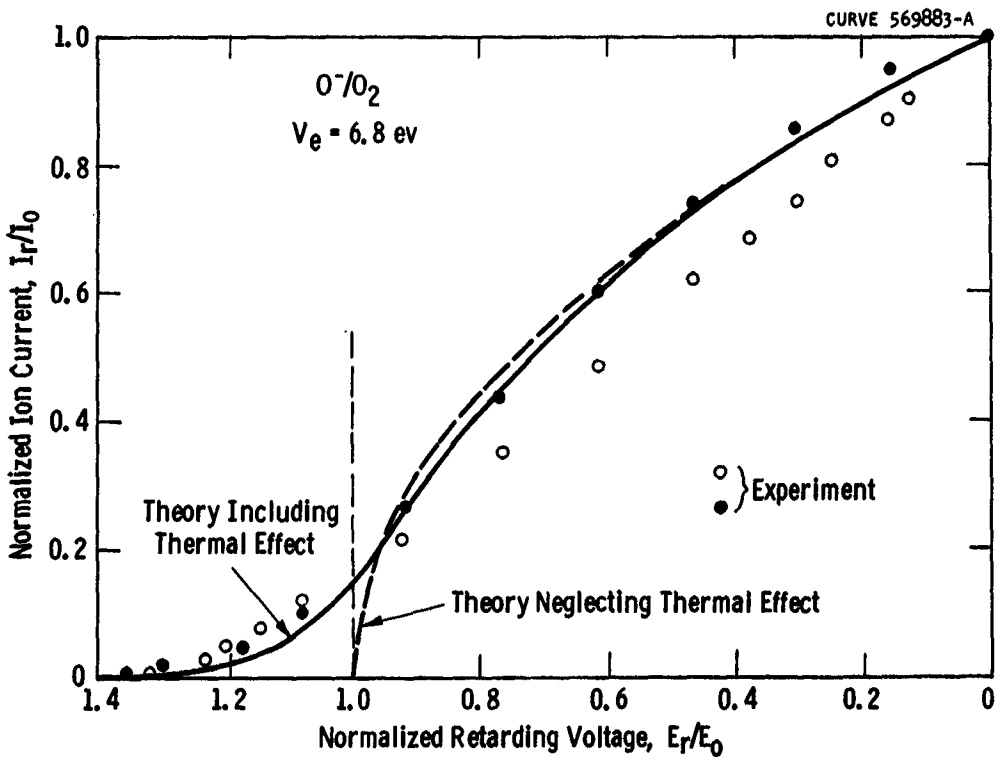

Fig. 1. Comparison of theoretical and experimental retarding curves for O^- from O_2 at an electron energy of 6.8 ev.

The normalized ion current is plotted against the ratio of the retarding voltage to ion kinetic energy. The two theoretical lines assume that the electrons are mono-energetic, the ion distribution is isotropic, and that D = 5.11 eV and A = 1.5 eV. Two sets of experimental data are shown: the closed circles are obtained at a high magnetic field ($\sim$1000 gauss) and relatively high pressure; the open circles are obtained at low magnetic field and relatively low pressure. The tubes used in the two experiments are slightly different. At the present time, no clear-cut choice can be made between the two experiments.

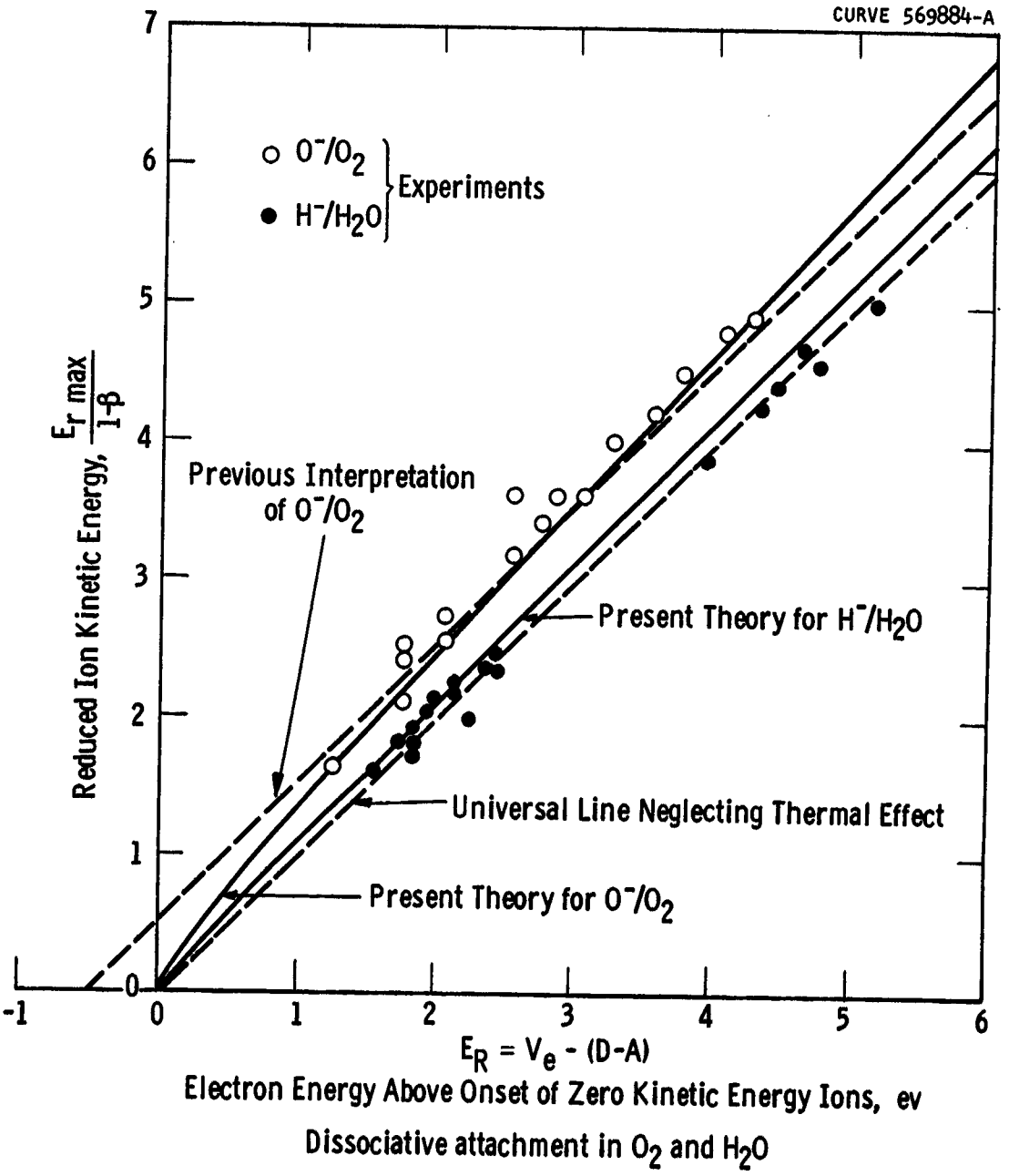
CURVE 569884-A
O^-/O_2
H^-/H_2O
Experiments
Previous Interpretation of O^-/O_2
Present Theory for H^-/H_2O
Universal Line Neglecting Thermal Effect
Present Theory for O^-/O_2
Reduced Ion Kinetic Energy, $\frac{E_{r\,max}}{1-\beta}$
$E_R = V_e - (D-A)$
Electron Energy Above Onset of Zero Kinetic Energy Ions, ev
Dissociative attachment in O_2 and H_2O

Figure 2